A description of the general effect of pH on formation of nitrate in soils[1]

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Summary – Zusammenfassung

Soil [H$^+$] and [OH$^-$] have a major effect on the rate of microbial mineralization of organic matter and the subsequent expression of nitrate-N (NO$_3^-$-N). The objective of this work is a mathematical description of the effect of [H$^+$] and [OH$^-$] on expression of NO$_3^-$-N from soil organic matter. Data obtained from the Cooperative States Research Service North Central Regional Committee-201 study were analyzed for effects of [H$^+$] and [OH$^-$] on expression of NO$_3^-$-N. Soil samples were collected in the 12-state Cornbelt Region (USA) during a 4-year period following a uniform protocol. Samples were taken immediately before or during planting and again at the V-5 growth stage of maize and analyzed for NO$_3^-$-N. The change in [NO$_3^-$-N] in the surface 0- to 30-cm of soil during pre-plant to V-5 growth stage of corn was estimated. Data were used only from sites receiving ≤ 15 kg N ha^{-1} as starter fertilizer. The change in [NO$_3^-$-N] was evaluated as a function of soil pH (usually obtained from 0- to 15- or 20-cm depth increments, the depth zone of probable formation). The data were examined as 1) the entire set and 2) only maximal values within a pH increment of 0.1 unit. The change in [NO$_3^-$-N] reached a maximum at a pH of about 6.7 ($\approx$ 200 nM [H$^+$]) and was negligible at pH < 5.0 or > 8.5. Application of a general energy model for limited systems showed greater sensitivity of NO$_3^-$-N production to [OH$^-$] than to [H$^+$]. Field observations show that gains of > 300 kg or losses of > 80 kg of NO$_3^-$-N ha^{-1} can occur in periods of about 60 days.
Key words: organic matter / nitrogen-mineralization-potential / US Cornbelt

Beschreibung des generellen Effekts des pH auf die Bildung von Nitrat in Böden

Die Bodenaktivitäten [H$^+$] und [OH$^-$] haben einen großen Einfluß auf die mikrobielle Mineralisierungsrate der organischen Substanz und die resultierenden Nitrat-N-Gehalte. Das Ziel dieser Arbeit ist eine mathematische Formulierung des Effekts von [H$^+$] und [OH$^-$] auf die Bildung von NO$_3$-N aus organischer Substanz. Dazu wurden Daten aus einer Studie des *Cooperative States Research Service North Central Regional Committee-201* analysiert. In dem aus 12 Bundesstaaten bestehenden „Cornbelt" (Maisanbauregion der USA) wurden während eines vierjährigen Zeitraums nach festgelegtem Verfahren Bodenproben entnommen. Diese Proben wurden unmittelbar vor oder während der Aussaat und erneut während der Wachstumsphase V-5 des Maises entnommen und auf NO$_3$-N analysiert. Die NO$_3$-N-Veränderung im 0–30 cm-Bodenbereich von der Vor-Aussaatphase zur V-5-Wachstumsphase des Maises wurde geschätzt. Es wurden Daten von Standorten verwendet, die ≤ 15 kg N ha^{-1} als Startdünger erhalten hatten. Die NO$_3$-N-Veränderung wurde als eine Funktion des Boden-pH-Wertes (der in der Regel in der Schicht von 0–15 oder 0–20 cm gemessen wurde, also in der Tiefenzone der wahrscheinlichen Nitratbildung) bewertet. Die Daten wurden 1) als Gesamtsatz und 2) nur als Maximalwerte innerhalb eines pH-Inkrements von 0,1 Einheiten untersucht. Die NO$_3$-N-Veränderung war bei einem pH von ca. 6,7 ($\approx$ 200 nM [H$^+$]) am größten und konnte bei pH < 5,0 oder > 8,5 vernachlässigt werden. Die Anwendung eines allgemeinen Energiemodells für begrenzte Systeme ergab eine größere Empfindlichkeit der NO$_3$-N-Produktion gegenüber [OH$^-$] als gegenüber [H$^+$]. Die im Feld gemachten Beobachtungen zeigten, daß Zunahmen von > 300 kg oder Verluste von > 80 kg von NO$_3$-N ha^{-1} in Perioden von ca. 60 Tagen auftreten können.

Introduction

Accumulation of nitrogen (N) by plants is critical to food production. For maize and cereal grass crops, the main form of uptake is nitrate-N (NO$_3^-$-N). A smaller fraction of N is accumulated as ammonium-N (NH$_4^+$-N). Work indicating the importance of NO$_3^-$-N to barley (*Hordeum vulgare* L.) production (*Soper* et al., 1971) led to further development of the NO$_3^-$-N soil test for maize (*Zea mays* L.). The very temporal nature of NO$_3^-$-N led to development of the pre-plant and pre-sidedress NO$_3^-$-N tests (*Magdoff* et al., 1984, 1990; *Binford* et al., 1992), which generally correlate well with grain production.

As a natural biological activity, production of NO$_3^-$-N is sensitive to a number of environmental factors such as temperature (for example, *Parker* and *Larson*, 1962; *Justice* and *Smith*, 1962; *Stanford* et al., 1975; *Honeycutt* et al., 1990), aeration (*Plummer*, 1916; *Amer* and *Bartholomew*, 1951; *Doran* et al., 1990; *Skopp* et al., 1990), nutrition and pH or [H$^+$]. Descriptions of effects of temperature and aeration have been provided (*Doran* et al., 1990; *Olness* et al., 1998). The importance of [H$^+$] to N-mineralization and NO$_3^-$-N production in soil has been

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known for some time and simple mathematical descriptions have been developed.

Studies of the effect of pH on production of NO_3^- fall in two general categories; those conducted with or without added N. The distinction is important because the natural process involves the production of NH_4^+ that is then oxidized to NO_3^- and each step is pH sensitive. Working with alkaline desert soils of pH > 7.2, *Martin* et al. (1942) concluded the apparent threshold/limit for mineralization appeared to be pH 7.7 and that at more alkaline pH values, net nitrification was not observed. The distinction of net nitrification is important because several early works with added NH_4^+-N indicated maximal rates of NO_3^--N production occurred between pH 8.0 and 9.0.

Cornfield (1952) studied production of NO_3^- in soils as a function of added chalk ($Ca/MgCO_3$) over a pH range of 4.37 to 8.13. He incubated soils with 1% added lime; neither post-treatment nor post-incubation pH values were given, but the upper limit of the pH values after addition of chalk was probably between 8.0 and 9.0. This work showed that the largest increases in NO_3^--N occurred in the most acidic soils and that little or no benefit was obtained from liming soils with pH $\geq$ 6.8. *Cornfield* (1960) also noted that the amount of N mineralized was closely correlated with NH_4^+-N released from soils on addition of hydroxide. *Weber* and *Gainey* (1962) found production of NO_3^- in acidic soils even at a pH of about 4.0; but, the rates were very slow ($\leq$ 0.32 µg N g^{-1} soil day^{-1}) relative to soils with pH values near neutrality. They found increases in the rate of NO_3^- production as the pH was adjusted to near neutrality. They also noted that production of NO_3^--N ceased in liquid cultures when the $[H^+]$ became > 10^{-6} M. Similarly, *Raison* et al. (1987) and *Honeycutt* et al. (1991) have shown rather slow nitrate formation for acidic soils in field studies. Working with near neutral soils, *Halvorson* and *Caldwell* (1948) showed that addition of lime to a Webster soil with pH about 6.5 resulted in decreases in the initial rates of NO_3^- production; the final pH values were 7.1.

Adding N to soils has two effects: 1) it increases the initial rate of NO_3^--N production and 2) the pH usually decreases upon incubation (for example, *Martin* et al., 1942; *Eno* and *Blue*, 1954). The acidifying process of nitrification tends to enhance rates of nitrification in systems with pH > optimum and inhibit it in systems with pH < optimum. Incubations of soil with added N show a general increase in the rate of NO_3^--N production as the $[H^+]$ decreases for acidic soils (*Dancer* et al., 1973). After addition of NH_4^+-N, *Eno* and *Blue* (1954) obtained the greatest rates of NO_3^--N production for soils remaining near neutrality during the incubation.

The mathematical description of the $[H^+]$ effect on NO_3^--N production remains only vaguely defined. *Dancer* et al. (1973) fitted a linear model to their data (NO_3^--N = $41.5 \cdot pH - 168.5$) over the range of pH 4.5 to 6.8; this has an intercept at about pH 4.1 but lacks an upper pH

limit. *Reddy* et al. (1979) used a segmented model to describe the nitrification of N from livestock wastes (NO_3^--N = $0.307 \cdot pH - 1.269$ for pH < 7.0, a constant rate from pH 7.0 to 7.4, and NO_3^--N = $-0.25 \cdot pH + 3.25$ for pH > 7.4). This model gives limits of NO_3^--N production at about pH 4.1 and 13.0. The limit on the acidic side agrees reasonably closely with data of *Weber* and *Gainey* (1962) and *Dancer* et al. (1973). The limit on the alkaline side may be a complex consequence of the large amounts of NH_4^+-N often present in livestock manures which can be readily nitrified even in environments with pH $\gg$ 7.0 and the acidification which nitrification causes rather than mineralization of soil N. Use of simple linear models to describe the effects of pH on nitrification implies an exponential relationship with $[H^+]$; however, these models are incapable of describing a maxima, minima, and optima as a continuous function of H^+ activity – a desirable aspect for computer models.

In laboratory incubations, the cumulative sum of NO_3^--N produced with time gradually approaches a limit and, hence, a potential production (*Stanford* and *Hanway*, 1955). Recognizing the effect of pH in development of the concept of a N mineralization potential (N_o), *Stanford* and *Hanway* (1955) periodically leached incubation vessels with a dilute salt solution to minimize effects of changes in pH during incubation on N mineralization. *Stanford* and *Smith* (1972) advanced the concept of a unique N_o for different soils. They essentially described a specific N_o, N_o^{sp} or existing potential. This N_o^{sp} can be differentiated from an intrinsic N_o^i; that is, that potential obtained when factors affecting mineralization are optimized. The distinction is useful in determining the relative cost:benefit ratios of modifying the microbial environment to change the rate of N-mineralization or nitrification.

This paper gives a mathematical description of the effect of $[H^+]$ and $[OH^-]$ on the expression of NO_3^--N formed in soils with only starter N additions ($\leq$ 15 kg N ha^{-1}) in the US Cornbelt.

Materials and methods

Cooperating scientists from the 12-state Cornbelt region (Ohio to Nebraska and Minnesota to Kansas) contributed observations following a uniform protocol (*Bundy* et al., 1999). The data set consists of contributions taken from > 300 sites having a range of soil textures and soil types and it includes a range of physical-chemical characteristics. Soil pH was recorded for only 226 observations. The [NO_3^--N] was measured to depths of both 30 cm and 60 cm at or just before planting and again when the crop reached the five-leaf growth stage. While the elapsed time between sampling ranged from about 21 to 90 days, the second sample was usually obtained about 50 to 60 days after the first sample.

Only data obtained from plots with $\leq$ 15 kg N ha^{-1} added as starter were used for modeling the pH effect. Starter fertilizer was often banded at a distance of 5 cm from the row and about 5 cm below the seed placement. Selection of plots receiving only starter was done to obtain estimates of NO_3^--N formation without perturbations from commercial sources of N.

Soil sampling followed a uniform protocol and this protocol avoided sampling the band applications of starter fertilizer N.
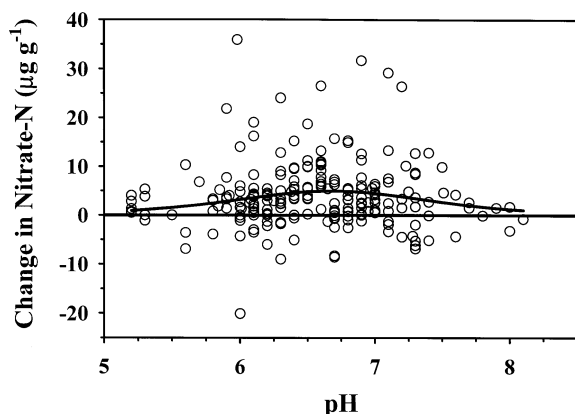
Soil pH was determined on a soil:water paste (1:2; *Thomas*, 1996). The $[NO_3^--N]$ in soil samples was determined on KCl extracts using calibrated standard procedures (*Mulvaney*, 1996) adopted by individual state experiment stations.

Initially, the data were fitted to an optimization model, a single variable $sech^2(pH)$ function (see appendix I) using the SAS PROC MODEL procedure (*Ray*, 1982) to obtain a general characterization of the data. Subsequently, maximal productions within a 0.1 pH unit were fitted to the general energy model for limited systems (GEMLS; Appendix II).
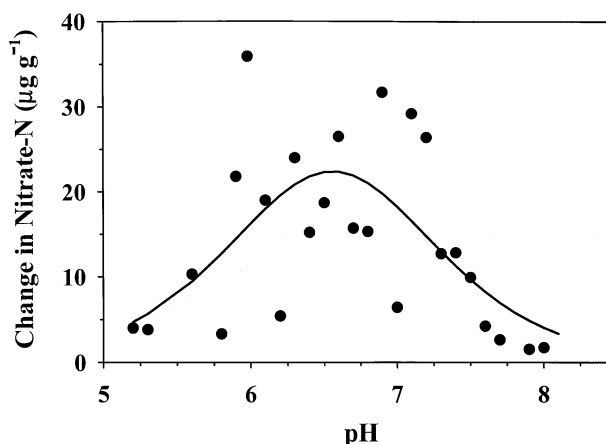
Results and discussion

The change in soil NO_3^--N concentration, $\triangle[NO_3^--N]\cdot\triangle t^{-1}$, as a function of pH for the 30-cm depth zone shows the variance expected for a naturally and biologically produced material (Fig. 1). The $[NO_3^--N]$ appears to reach a maximum in the pH range 6.5 to 7.0. The data also show an almost symmetrical pattern. This indicates that an increase or decrease in pH from the maximum has a nearly identical effect even though it is a logarithmically-scaled value.

In many instances, the $\triangle[NO_3^--N] \cdot \triangle t^{-1}$ was negative, indicating a net loss of NO_3^--N over the brief sampling interval. Because NO_3^--N is a product of microbial acitvity that is almost entirely dependent on organic residues for a source of energy, most NO_3^--N is produced in the upper 15-cm depth zone of the soil. Because it is very soluble in water, it is easily leached to lower depths and net losses are expected in areas where the amount of rainfall infiltration is large. Immobilization is discounted because tillage was usually done in the fall, so residues would have begun to decompose before the PPNT (drought instances excepted). Plant uptake accounts for about 30 to 40 kg N ha^{-1} (10 to 12 g $plant^{-1}$, 4.25 to 4.5% N, and about 6 to 7 plants m^{-2} or an equivalent of 3.5 to 5.0 $\mu g\ g^{-1}$ in a 60-cm

Figure 2: Maximal change in concentration of NO_3^--N within a 0.1 pH value increment in the 0- to 30-cm depth increment for Cornbelt soils as a function of pH (n = 25). The solid line represents a $sech^2(pH)$ model estimate of $[NO_3^--N]$. (Reprinted with permission: *Olness* et al., 1977. Chapt. 5. Biosolids and their effects on soil properties. pp. 141–165. In Handbook of Soil Conditioners. R. E. Terry, ed. pub. Marcel Dekker, New York).
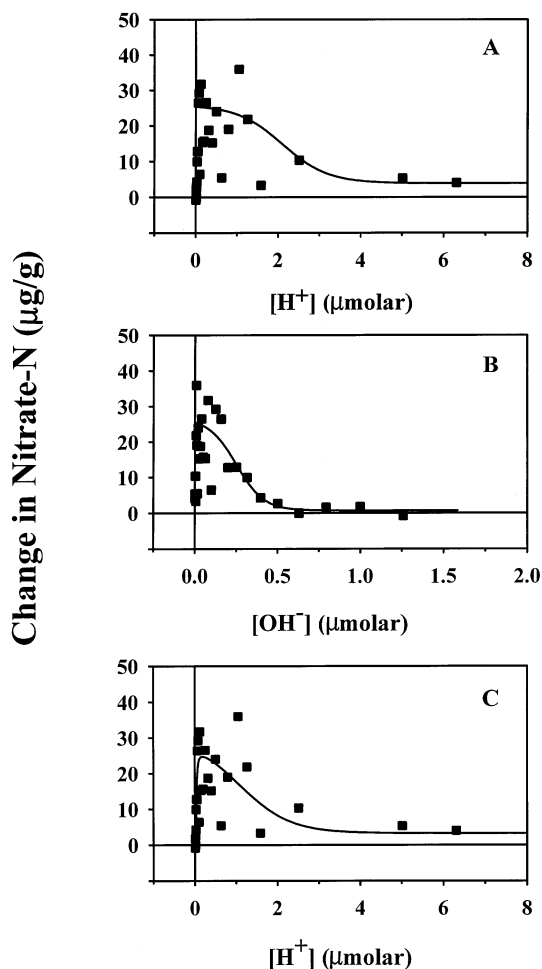
Abbildung 2. Maximale Veränderung der NO3-N-Konzentration innerhalb einer 0,1 pH-Spanne in der 0–30 cm-Schicht von Böden der Cornbelt-Region der U.S.A. als Funktion des pH (n = 25). Die Kurve entspricht der NO3-N-Schätzung nach einem $sech^2(pH)$-Modell (s. Appendix I).

depth increment). Starter fertilizer could supply about 30 to 50% of the plant uptake.

By comparing the soil NO_3^--N concentrations in the 0- to 30-cm depth zone with that in the 0- to 60-cm depth zone an estimate of the leaching intensity is obtained. About 8.5% of the sites showed a net loss of NO_3^--N from a 60-cm profile between the preplant and pre-sidedress sampling dates. Some sites showed changes in the 30- to 60-cm zone and for others, losses of NO_3^--N may have been less than the nitrification gains between sampling dates. When data accessions with obvious leaching of NO_3^--N between sampling dates were excluded, an optimal pH of about 6.7 was indicated (data not shown).

When only maximal values within a pH increment (for example, 6.60 to 6.69) are considered, a very pronounced effect of pH on accumulation of NO_3^--N is evident (Fig. 2). Even in this last data set, plant removal and some leaching of NO_3^--N have undoubtedly occurred. Still, regardless of the discriminating criteria applied to the data set, the indicated optimal pH varied within a very narrow range from about 6.5 to 6.7.

After conversion of pH values to $[H^+]$ and $[OH^-]$, the data were fitted to a GEMLS (general energy model for limited systems, *Olness* et al., 1998; see appendix II). When the data are plotted as a function of $[H^+]$ rather than as pH, the effect is easily visualized (Fig. 3a). If $[H^+]$ was the only factor inhibiting NO_3^--N formation through mineralization and nitrification activity, the rate of nitrification would approach zero as the $[H^+]$ increased and a maximum as the $[H^+]$ decreased. However, observation of a maximal rate of nitrification at a concentration of about 200 nM $[H^+]$ recognizes that both $[H^+]$ and $[OH^-]$ are affecting the system.

Figure 1: Change in concentration of NO_3^--N in the 0- to 30-cm depth increment for Cornbelt soils as a function of pH (n = 223). The solid line represents a $sech^2$ (pH) model estimate of $[NO_3^--N]$.

Abbildung 1: Veränderungen der NO3-N-Konzentration in der 0–30 cm-Schicht von Böden der Cornbelt-Region der U.S.A. als Funktion des pH (n = 223). Die durchgehende Kurve entspricht der NO3-N-Schätzung nach einem $sech^2(pH)$-Modell (s. Appendix I).

Figure 3: a) Maximal changes in soil [NO$_3^-$-N] as a function of [H$^+$]. The solid line represents a model estimate of [NO$_3^-$-N] at [H$^+$] > 200 nM (n = 25) using only [H$^+$] as a variable. **b)** Maximal changes in soil [NO$_3^-$-N] as a function of [OH$^-$]. The solid line represents a model estimate of [NO$_3^-$-N] at [OH$^-$] > 5 nM (n = 25) using only [OH$^-$] as a variable. **c)** Maximal changes in soil [NO$_3^-$-N] as a function of [H$^+$]. The solid line represents model estimates of the combined effects of [H$^+$] and [OH$^-$] on [NO$_3^-$-N] production; the model has an R^2 = 0.530 (n = 25).
Abbildung 3: a) Maximale Veränderungen des Boden-NO$_3$-N als Funktion der [H$^+$]-Aktivität. Die Kurve entspricht einer Modellschätzung von NO$_3$-N bei [H$^+$] > 200 nM mit [H$^+$] als alleiniger Variablen (n = 25). **b)** Maximale Veränderungen im Boden-NO$_3$-N als Funktion von [OH$^-$]. Die Kurve entspricht einer Modellschätzung von NO$_3$-N bei [OH$^-$] > 5 nM (n = 25) mit [OH$^-$] als alleiniger Variablen. **c)** Maximale Veränderungen des Boden-NO$_3$-N als Funktion von [H$^+$]. Die Kurve entspricht einer Modellschätzung der kombinierten Wirkungen von [H$^+$] und [OH$^-$] auf die NO$_3$-N-Produktion (r^2 = 0,530; n = 25).

The indicated concentration for maximal NO$_3^-$-N production in the absence of added N (starter N ignored) occurred at 200 to 250 nM [H$^+$]. This is much greater than the range given by *Reddy* et al. (1979) of 40 to 100 nM [H$^+$]. It is also far greater than the optimal estimates of 1 to 10 nM [H$^+$] cited for nitrification (see *Martin* et al., 1942).

A plot of △[NO$_3^-$-N] as a function of [OH$^-$] gives a relationship analogous to that obtained for [H$^+$] with the important exception of a much steeper slope (Fig. 3b). Thus, once the system becomes more basic than optimal

(about 200 nM [H$^+$]), expression of NO$_3^-$-N becomes more severely inhibited than that which occurs with an equivalent increase in [H$^+$].

Typically, this region realizes about 1 to 2 mm of evaporative water loss daily in the spring; this water loss rate increases to about 6 mm per day with transpiration after canopy closure. A loss of 1 µg mL^{-1} of NH$_3$ in the evaporated water would result in a loss of < 2 kg N ha^{-1} during the sampling interval. At a pH nearer the pK$_b$ of 4.76 at 20°C ($\approx$pH 9.24) the potential evaporative loss of NH$_3$ generated through mineralization of organic matter becomes more important. Because a) the [NH$_4^+$-N] is usually small (on the order of mmolar), b) NH$_4^+$-N is rapidly converted to NO$_3^-$-N, and c) most of the soils sampled were medium to fine textured, losses from this pathway were ignored as a factor in the model.

The asymmetry of rate response seems a general consequence of an optimum which occurs at [H$^+$] > 100 nM. Because of the dissociation constant of water, it is customary to discuss either [H$^+$] or [OH$^-$] but not usually address both in questions of acidity/basicity. It is generally assumed that determining the concentration of one is sufficient and both are known. However, treating each individually suggests a unique effect on the nitrification enzyme system; that is, that each ion exerts an independent effect. By combining the two GEMLS descriptions of the effect of [OH$^-$] and [H$^+$] into a single expression, we describe the change in rate of nitrification effected by a small change in both [OH$^-$] and [H$^+$]:

$$\triangle[NO_3^--N] \cdot \triangle t^{-1} = a \cdot (b - \{(e^{k([H^+]-E)} - e^{-k([H^+]-E)}) / (e^{k([H^+]-E)} + e^{-k([H^+]-E)})\}) - \alpha \cdot (\beta - \{(e^{K([OH^-]-\phi)} - e^{-K([OH^-]-\phi)})/ (e^{K([OH^-]-\phi)} + e^{-K([OH^-]-\phi)})\}).$$

This model gives a relatively good representation of the relationship of [NO$_3^-$-N] to [H$^+$] and [OH$^-$] (Fig. 3c; R^2 = 0.530). Considering the large number of factors affecting the expression of NO$_3^-$-N over the sampled region, the R^2 is rather large. Each parameter/coefficient is unique (Tab. 1). The coefficients k and *K* and the critical values *E* and ϕ are relatively stable. Assuming that plant uptake of N was almost entirely as NO$_3^-$-N formed through mineralization and adding this amount to that observed in the soil causes the a, α, b, and β values to change slightly (Tab. 1).

The model describes a general nature of the effect of [H$^+$] and [OH$^-$] on the rate of production of NO$_3^-$-N. More rigorous definition and constraint of the variables is needed to describe the *in situ* rates of NO$_3^-$-N production. It is expected that the parameters generated will be reasonable estimates of those obtained from observations in controlled studies. The current model provides an estimate of the practical effect of modifying pH on the supply of NO$_3^-$-N from soil organic matter to the growing crop.

Expression of [H$^+$] as pH obscures the complexity of N transformations in the natural environment and hinders visualization of the nature of complex interactions at the

Table 1: Approximate parameter and variable values for the combined $[H^+]$ and $[OH^-]$ General Energy Model for Limited Systems.
Tabelle 1: Ungefähre Werte von Parametern und Variablen für das allgemeine kombinierte $[H^+]$- und $[OH^-]$-Energiemodell für begrenzte Systeme.

Energy Form	coefficients		External Effects	Critical Values
	Model	Energy		
	$\mu g\ g^{-1}$ soil	$\mu mole^{-1}$		$\mu mole$
Observed in soil				
$[H^+]$	a, 14	k, 0.8	b, 0.0	E, 1.05
$[OH^-]$	α, 14	κ, 7.0	β, 0.3	ϕ, 0.24
Adjusted for plant uptake				
$[H^+]$	a, 13.3	k, 0.77	b, 0.41	E, 1.05
$[OH^-]$	α, 11.4	κ, 7.0	β, –0.01	ϕ, 0.24

molecular scale. The suggestion of an optimal pH value does not preclude the existence of several unique N transforming populations each having an optimal pH value; such suggestions have been noted (*Ishaque* and *Cornfield*, 1972). Here however, within all microbial populations mineralizing N, an optimal pH appears to exist at which $\triangle[NO_3^- \text{-N}] \cdot \triangle t^{-1}$ is maximized.

By setting the limit of N mineralization at an optimal pH of 6.7 equal to 100%, the function can be used as a scaling coefficient of N_o^i; for example:

$$f(H^+, OH^-) \cdot N_o^i \cdot f(X_i) = N_o^{sp}$$

where $f(X_i)$ represent other scaling functions affecting mineralization such as temperature, aeration, mineral nutrition, etc. This approach enables an evaluation of the cost of modifying soil pH, for example, by application of lime, and the relative gain in NO_3^--N due to enhanced N-mineralization. Recognizing, of course, that N-mineralization is one of several processes/variables affected by a change in pH.

The estimate of the optimal pH was developed independently of other variables known to affect microbial respiration and N-mineralization such as relative aeration, bulk density, soil texture, soil organic matter content, time, or mineral nutritional status. That a relationship is apparent in the result testifies to the importance of $[OH^-]:[H^+]$ in the mineralization of N from soil organic matter and production of NO_3^--N.

Which comes first: An optimal pH for nitrification or an optimal pH for sequestration of soil organic matter, the source of mineralizable N? The question is often posed "because soils that have pH near neutrality often have greater organic matter content and because organic matter is the source of N, wouldn't you expect to see an optimal pH for NO_3^--N formation near neutrality?" To explore this question thoroughly, we need data sets of soils with similar textures each having a range of organic matter contents and a range of pH values. The textural consideration is important because it determines the water-holding capacity and, as a consequence, the relative aeration. The data set in Fig. 2 had an organic matter content range of 1.95% to 4.5% and a mean of 3.31%. Because the range of organic matter was rather small, maximal NO_3^--N production was poorly correlated with

organic matter (NO_3^--N = 2.08 + 3.64·OM; $R^2 \leq 0.1$). So, any effect of the concentration of organic matter on nitrification seems modest. Only agriculturally important soils were surveyed and, perhaps as a consequence, the range of organic matter for all sites was only about 0.7% to 6.7%. Frequencies of the extreme concentrations of organic matter were very small. The results suggest that, because N is the most often limiting element, more organic matter is generated and subsequently sequestered at a pH near neutrality because the environment favors nitrification at that pH rather than vice versa.

The optimal pH suggested in this data set appears to have support in past studies (Figs. 3a and b). Because the data from the literature were extracted from rather disparate studies, NO_3^--N production was placed on a relative scale with the greatest rate in each report set at 1.0. When the model is applied to these studies, the optimal $[H^+]$ is about 300 nM – a value not much different from that obtained in the Cornbelt soils. Data taken from the literature are somewhat biased relative to data analyzed here because treatments were imposed and, in some cases, measurements were made on laboratory incubations. In many cases, pH changed during the study and patterns of nitrification are ignored (see *Morrill* and *Dawson*, 1967).

The regional report notes that medium textured soils (loams, silt loams), soils where alfalfa was the previous crop, and those in which manure was applied in the study year were likely to show the greatest increase in NO_3^--N (*Bundy* et al., 1999). In the final data set (n = 25), alfalfa was a previous crop on the soils having pH 6.6, 6.7, and 6.9; this produces a slightly larger maximal value than would have been produced if non-leguminous crops had been grown the previous year. The mean elapsed time between samplings in this set was about 55 days.

It is not surprising that over half of the observations in the last data set come from silt loam soils. These soils have the greatest potential available water content and thus are able to accomodate infiltration of more rainfall without leaching than coarser or finer textured soils.

In the natural environment, production of and loss of NO_3^--N within a 60-cm profile can be quite large (Fig. 1). Gains of > 300 kg NO_3^--N ha^{-1} were observed within as little as 60 days when climatic and soil environmental
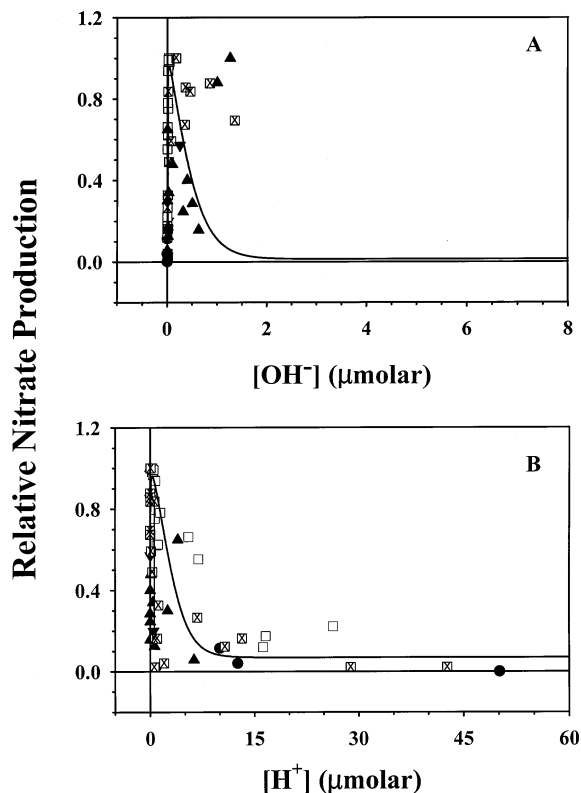
Figure 4: a) Changes in soil [NO₃-N] given in various literature sources as a function of [OH⁻]. **b)** Changes in soil [NO₃-N] given in various literature sources as a function of [H⁺]. Symbols in both panels are as follows: □, *Dancer* et al., 1973; ⊠, *Cornfield*, 1952; ▲ ▼ ●, *Frederick* and *Broadbent*, 1966 (citing several studies).

Abbildung 4: a) Veränderungen des Boden-NO₃-N als Funktion des [OH⁻] nach verschiedenen Literaturangaben. **b)** Veränderungen des Boden-NO₃-N als Funktion des [H⁺] nach verschiedenen Literaturangeben. Symbole in beiden Graphiken: □ *Dancer* et al. (1973), ⊠ *Cornfield* (1952), ▲ ▼ ● *Frederick* und *Broadbent* (1966, mehrere Untersuchungen).

conditions were near optimal (*Bundy* et al., 1999). Losses of > 80 kg NO_3^--N ha^{-1} occurred within the same period of time when rainfall infiltration exceeded the water-holding capacity of the soil. This huge potential variation in production of NO_3^--N poses a challenge to natural resource managers because the time span available for imposition of management decisions is very brief. Adjustment of soil pH offers an additional tool for management of NO_3^--N production in the natural environment.

Conclusions

Observations obtained from soils in the US Cornbelt indicate maximal production of NO_3^--N in soil at a pH of about 6.7 (200 nM [H⁺]). Results of the regional study suggest that part of the variation observed in natural NO_3^--N production seems explained by a complex effect of both [H⁺] and [OH⁻] on microbial activity and subsequent nitrification. The model developed from the regional data suggest little or a slower rate of production of NO_3^--N at pH values < 5.0 or > 8.0. Under rather acidic or

calcareous conditions, fertilizer-N may achieve more consistent efficiency than soils with near neutral soil pH values.

Between pH values of about 6.0 to 7.5, variance in natural production of NO_3^--N leads to variable N fertilizer use efficiencies and greater risks of environmental pollution. Potential demand of many crops for NO_3^--N on many soils is sometimes met through natural production. For such soils, testing for [NO_3^--N] and application of appropriate amounts of fertilizer-N should improve N-use efficiency.

Generally, because of the intensity of the relationship between [OH⁻] and NO_3^--N production, greater gains in production rates of NO_3^--N from soil organic matter appear achievable by adjustment of pH from values > 7.5 to 6.7 than in adjustment of pH from values of < 6.0 to 6.7.

Acknowledgement

Appendix I

The derivative of the general energy model for limited systems with respect to time, the sech²(X-E), describes a optimization function:

$$\triangle Q \cdot \triangle t^{-1} = b \cdot (e^{(k(X-E))} + e^{-(k(X-E))})^{-2},$$

where $\triangle Q$ = the change in a quantity, b = a function coefficient describing the maximal expression, e = the natural logarithmic base (2.718), k = the energy coefficient and E = that energy intensity at which $\triangle Q \cdot \triangle^{-1}$ is maximized. While this function provides a general description of the pH data, an exponential expression of pH has little explanatory value. A simple quadratic function appears equally capable of describing the optimal pH, but suffers the same defect.

Appendix II

All biological systems must be viewed as limited systems. That is, the amount of energy which can be transformed within a unit of time has a limit. The general energy model for limited systems provides a description of the effect of increasing energy intensity on an organism expressing deficiency in intensity of, or response to, the energy form. The form of energy can be electromagnetic (visible and ultraviolet photosynthetically active radiation; infra-red or thermal radiation; *Olness* et al., 1990 a and b; *Olness* et al., 1991), or chemical (*Olness* et al., 1995). This model, a synthesis of the concepts of Arrhenius and later of *Mitscherlich* (1930), accommodates systems/organisms which have limited accretion potential. The mathematical model is:

$$Q_t = a \cdot (b + \{(e^{k(X-E)} - e^{-k(X-E)})/(e^{k(X-E)} + e^{-k(X-E)})\}).$$

The intensity of the energy form is represented by X. The activation energy of the Arrhenius model, E, represents the point at which increasing concentrations result in continually decreasing marginal gains in relative rate or yield. This can also be considered a critical concentration. Historically, much attention has been focused on those systems in which $X > E$. The coefficient of the energy form, k, is a composite of other energy intensities interacting within/on the system. The coefficient 'a' represents the maximal expression that can be achieved by the organism under the constraints of other energy forms. The coefficient 'b' accommodates relative versus absolute scales of energy and incidental or external contributions to the total. Here, b includes contributions of NH_4^+–N from rainfall, plant uptake, autotrophic N_2 fixation, etc.

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